

Methanol and Carbon Monoxide Production from Natural Gas

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INTRODUCTION

Partial oxidation of methane to methanol and formaldehyde holds considerable potential for producing liquid fuels and petrochemicals from natural gas. Several groups (Burch et al., 1989; Gesser et al., 1985 and 1987; Hunter et al., 1990; Varlagadda et al. 1988) have investigated homogeneous partial oxidation. Various sensitizers were capable of lowering the partial oxidation reaction temperature (Hunter et al., 1987, 1990). For most of the literature cited, the methanol selectivity varies from 20 to 80 percent. Some research groups have stated that it is difficult to obtain consistent results for the direct conversion of methane into methanol. In this study we present data illustrating the importance of the closure of the oxygen balance, the effect of materials of construction and type of reactor on the yields and selectivity of methanol. A kinetic model containing 175 homogeneous free radical reactions was developed and is used to simulate the performance of a plug flow reactor. Helton (1991) presents additional details on this study.

EQUIPMENT

Two reactor systems are utilized research to study the effects of reactor design on methane activity and product selectivity. Reactor system I can be operated from 1 - 100 atmospheres at temperatures between 25 and 450 °C. Non-selective catalytic wall effects are minimized by using a Pyrex liner. The tubular reactor and Pyrex liner is described in Figure 1. All tubing, exposed to temperatures above 180 °C contains an inner lining of fused silica in order to minimize the potential for surface reaction. For this system the feed is mixed and flows over several feet prior to entering the heated reactor zone of 400+ °C. In the reactor zone it is partial heated prior to entering the reactor tube through the 90 ° elbows. The elbows are 316 stainless steel and a portion of the SS is exposed to the reactants at high temperatures. Some or possibly even substantial reaction may have occurred in this section of the reactor.

Reactor system II is a commercial unit constructed by Autoclave Engineers, and is the Model 900 Micro-Scale Bench-Top Reaction System including the chromatographic system. Three basic modules comprise the reactor system: reactor, control, and analytical modules. A temperature controlled oven encloses the reactor system. Figure 2 provides a detailed description of the tubular reactor. For this system the gases are mixed at 180 °C and pass through an array of valves prior to entering the end of the reactor tube at 180 °C. No reaction occurs below 300 °C. As the fluid flows through the reactor tube it is heated by the three zone heater. The reaction is not conducted under isothermal conditions in either system, so that temperatures reported herein are the maximum temperatures of the reaction mixture. The analytical system

consists of an AE computer-controlled high-performance gas chromatograph containing a capillary and three packed columns along with a palladium transfer tube for hydrogen detection. Detailed operating procedures for the AE 900 Micro-Scale Bench-Top Reaction System exists in the manufacturer's operations manual.

The differences in the two reactor systems is the exposure of SS in the inlet elbows of Reactor System I and the possibility of reaction in this inlet section. Reactor System II has a straight section and no exposure of the reactants to SS as the reactants are heated to the reaction temperature. Also, with the AE-MSBTR instantaneous instead of time average material balances could be obtained.

RESULTS AND DISCUSSION

Burch et al. (1989) concluded the reason the high selectivity work of Gesser et al. (1987) could not be reproduced was due to small, but possibly important, differences in the design of the reactor. Burch and co-workers believed the methane to methanol gas-phase reaction operated within essentially unsteady-state conditions. Gesser et al. (1987) states that the reaction can occur under cool flame conditions in certain temperature and pressure regions. Also, the degree of pre-mixing of the reactant gases may have influenced the high selectivities reported.

Although the product distribution may be affected by the type of experimental apparatus, non-steady state conditions, or gas pre-mixing, failure to close the atom balances may explain the discrepancies in the range of selectivities observed in previous work. Figure 3, which was generated by using Monte Carlo simulation for a feed containing methane and 2.3% and 9.4% oxygen, respectively, illustrates the importance in closing carbon and oxygen atomic balances. For a feed containing 2.3% oxygen and 97.7% methane, a deviation in the carbon atom balance closure of 1% could result in 12 percentage points error in the methanol selectivity.

Table 1 illustrates that the addition of 5 percent ethane to the reaction mixture does not alter the methanol selectivity. However, the reaction temperature is lowered approximately 20 °C. Thus, ethane is capable of initiating the generation of free radicals more readily than methane which leads to further oxidation and enhances the formation of methanol at a lower temperature.

Figure 4 compares the methanol selectivity for the TEHBTR and AE-MSBTR reactor systems. The initial oxygen concentration was varied from 4.3 percent to 10.0 percent. Table 2 lists the gas hourly space velocity and reactor residence time for each reactor system. Except for one experiment, the residence time was maintained at approximately 17 seconds by varying the space velocity at each reaction pressure. The total pressure ranged from 20 to 50 atmospheres. Figure 4 indicates that methanol reaches a maximum after 20 percent of the oxygen is converted. The methanol selectivity could not be increased above 35 percent despite the range of oxygen concentrations and total pressures studied. There is an increase in methanol selectivity to 42 percent for reactor system TEHBTR, but this only occurred at an oxygen concentration of 4.3 percent, 20 atmospheres pressure, and a residence time of approximately 6 seconds.

The walls of the TEHBTR system appear to be catalytically active. When the total pressure is increased from 20 to 50 atmospheres the methanol selectivity decreases drastically from 30 to approximately 10 percent. If the partial oxidation of natural gas was purely homogeneous an increase in reactor pressure should minimize any surface reactions since the gas density to reactor wall surface is greater. Since the opposite is observed, the walls in the TEHBTR system must be catalytically active.

Few kinetic models for the homogeneous partial oxidation of methane to methanol have appeared in the literature. Onsager et al. (1989) and Durante et al. (1989) presented gas phase models at the International Chemical Congress of Pacific Basin Societies for the low temperature partial oxidation of methane to methanol. Onsager's reactor consisted of a one-chamber reactor with an alumina and stainless steel inner surface. The main part of the reaction rate parameters were taken from Tsang (1987) and Tsang and Hampson (1986). Some reactions were generated by Onsager et al. (1989) without any reference to literature values. The rate parameters of these reactions were estimated on the basis of analogous reactions.

Durante et al. (1989) constructed a kinetic model for the homogeneous gas phase reactions involved in methane partial oxidation utilizing published rate constants and activation parameters by Bedeneev et al. (1988). The model predicted the experimental findings of Yarlagadda et al. (1988) for runs at low temperature and oxygen partial pressures, but it could not reproduce the high methanol selectivities (exceeding 80 percent) reported at an 8 percent methane conversion. Onsager et al. (1989) and Durante et al. (1989) limited their models to the reaction of methane and oxygen. Thus, it was necessary to develop a model which incorporated the combined reactions of methane and ethane with molecular oxygen.

A kinetic model consisting of 175 free radical reactions was developed to simulate the reported experimental results. Pre-exponential constants for five reaction steps were increased above the recommended literature values in order to predict the experimental data. The pre-exponential constants were multiplied by the factors illustrated in Table 3. The published rate constants for these two reactions were estimated from the analogous reaction of formaldehyde with molecular oxygen. The increased pre-exponential constants for the formation of carbon dioxide is within the uncertainty of the literature values. Figure 5 shows a comparison of model predictions with experimental data. The kinetic model predicts the experimental data with remarkable accuracy.

CONCLUSIONS

Oxygen atom balance closure is needed to insure a minimum error in the calculated methanol selectivities, because it is the limiting reactant when excess methane is used. Large deviations in products selectivities can occur even though the overall material and the carbon atom balance closures are satisfied to a $\pm 2\%$.

The proposed kinetic reaction mechanism is capable of predicting the homogeneous reaction of methane and ethane with molecular oxygen. The model accurately predicts the product selectivities and conversions for the range of experiments in this investigation.

Additional cracking reactions need to be added to the mechanism in order to predict higher ethylene selectivities at low oxygen conversions (less than 10 percent). This would lower the predicted formaldehyde selectivity at low conversions and help in predicting the formaldehyde selectivity more accurately. Also, some spectroscopic work could be performed to determine the free radical concentrations during the reaction. Since the free radicals appear to reach a pseudo steady state, spectroscopic instruments may be able to observe and quantify these species. This would help in improving the kinetic model.

ACKNOWLEDGEMENT

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Table 1: Effect of Ethane on Reaction Temperature and Methanol Selectivity

94 % Methane		89 % Methane - 5 % Ethane	
Reaction Temperature (°C)	Methanol Selectivity	Reaction Temperature (°C)	Methanol Selectivity
413	33.3	388	36.1
421	33.4	390	34.7
429	31.8	398	31.0
421	33.9	401	32.5
414	34.3	405	32.0

Table 2: Experimental Conditions for TEHBTR and AE-MSBTR

Reactor Conditions	Unit	Space Velocity, hr ⁻¹	Space Time, seconds
4.3% Oxygen 20 atm	TEHBTR	4652	5.9 - 6.3
6.35% Oxygen 50 atm	AE-MBTR	4165	16.4 - 17.9
8.20% Oxygen 20 atm	AE-MBTR	1573	17.9 - 18.8
9.40% Oxygen 50 atm	AE-MBTR	4165	17.2 - 17.6
9.70% Oxygen 50 atm	TEHBTR	4200	18.0 - 18.9
9.70% Oxygen 50 atm	AE-MBTR	4165	17.5 - 17.7
10.0% Oxygen 50 atm	TEHBTR	4104	18.2-19.0

Table 3: Enhancement Factors for the Pre-exponential Constants

Reaction	Enhancement Factor
$\text{CH}_4 + \text{O}_2 = \text{CH}_3 + \text{HO}_2$	1.0×10^7
$\text{C}_2\text{H}_6 + \text{O}_2 = \text{C}_2\text{H}_5 + \text{HO}_2$	7.0×10^6
$\text{CO} + \text{CH}_3\text{O} = \text{CH}_3 + \text{CO}_2$	3.5
$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	3.5
$\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$	3.5

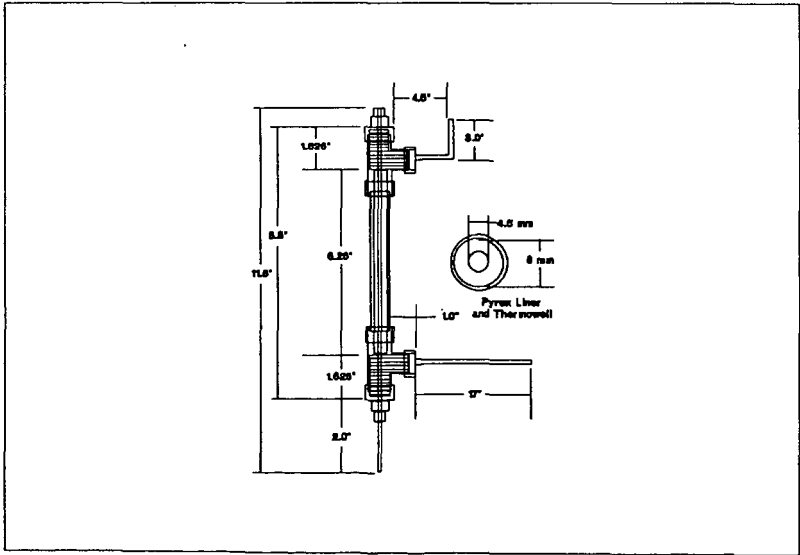


Figure 1: TEHBTR-Reactor Dimensions

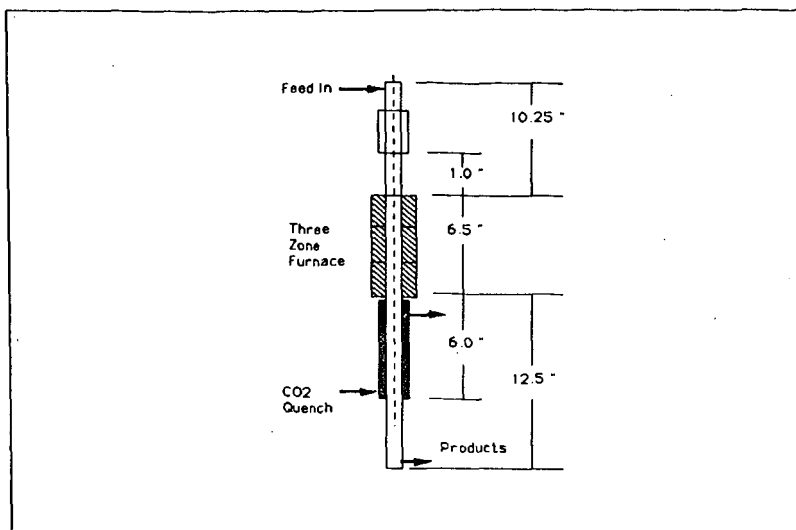


Figure 2: AE-MSBTR-Reactor Dimensions

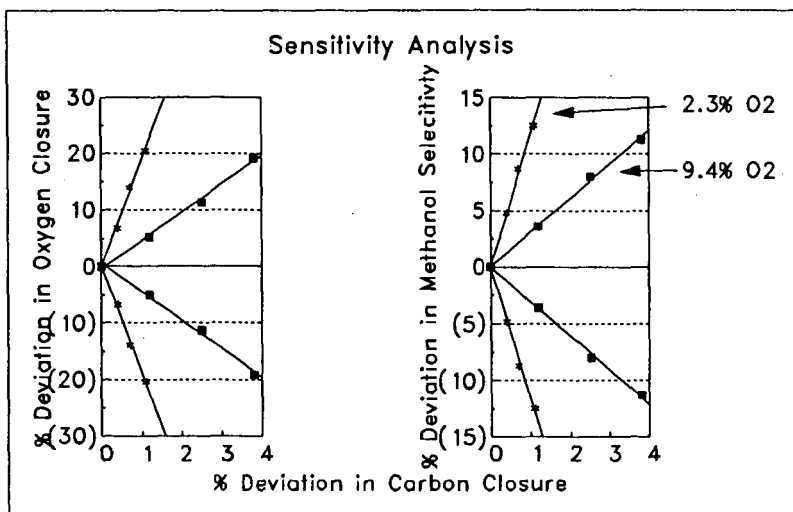


Figure 3. Monte Carlo Sensitivity Analysis (Oxygen feed concentrations of 2.3% and 9.4%)

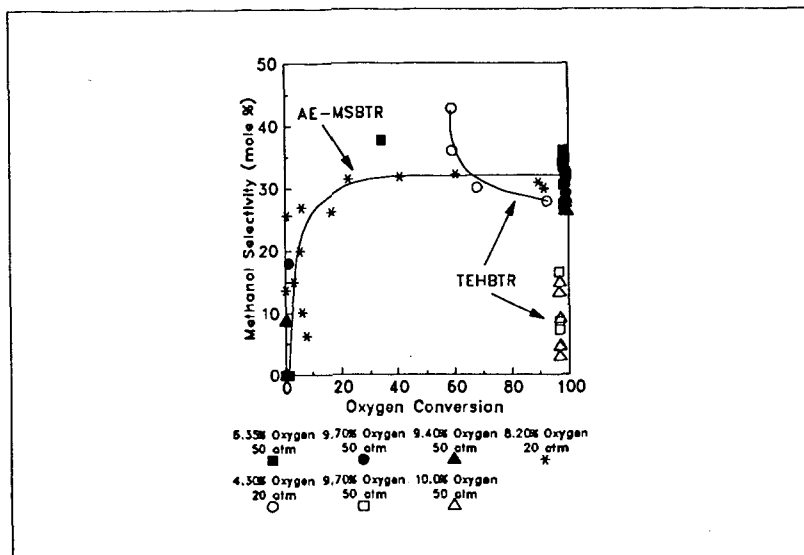


Figure 4: Methanol Selectivity for the Thermal Partial Oxidation of Natural Gas

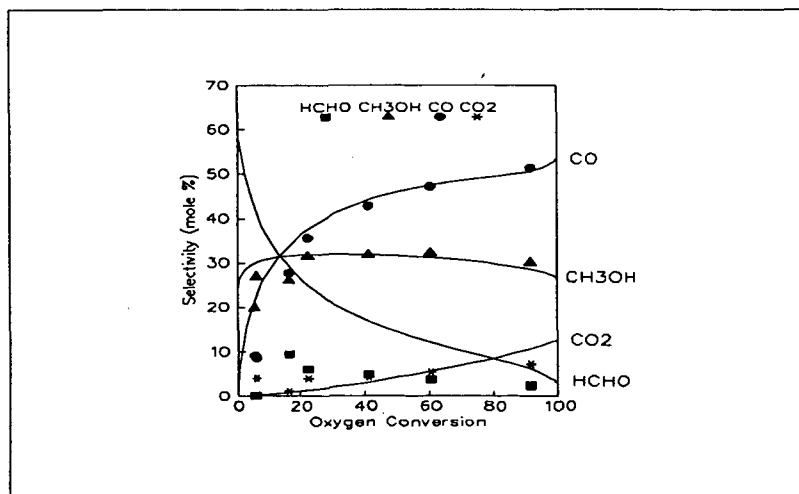


Figure 5: Comparison of Model Selectivity Predictions and Experimental Data for the Partial Oxidation of Natural Gas (8.2 % Oxygen, 5.1 % Ethane, 86.7 % Methane, Pressure = 20 atmospheres, Space Velocity = 1573 hr⁻¹)